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Oxygen isotope equilibrium in brachiopod shell fibres in the context of biological control

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Introduction

With their long geological history and stable low-Mg calcite shells, *Rhynchonelliform* brachiopods are attractive sources of environmental data such as past seawater temperature (Buening and Spero, 1996; Auclair *et al.*, 2003; Brand *et al.*, 2003; Parkinson *et al.*, 2005). Concerns about the influence of vital effects on the stable isotope composition of brachiopod shells (Popp *et al.*, 1986), led to isotope analyses of different parts of brachiopod shells in order to identify those parts of the shell that are influenced by any vital effect and those parts that may be suitable recorders of seawater temperature *via* stable oxygen isotope composition (Carpenter and Lohmann, 1995; Parkinson *et al.*, 2005). Such detailed studies demonstrated that the outer primary layer of acicular calcite is isotopically light in both $\delta^{18}O$ and $\delta^{13}C$ while the secondary layer, composed of calcite fibres, is in oxygen-isotope equilibrium with ambient seawater (Fig. 1) (Parkinson *et al.*, 2005). Use of the isotopically-light primary layer calcite in temperature calculations would result in seawater temperatures that are significantly higher than the actual ambient seawater temperature (Parkinson *et al.*, 2005). Isotopic equilibrium between ambient seawater and secondary layer calcite is attained while biological processes exert strict control on all aspects of shell formation. This biological control is evident in the morphology and juxtaposition of the calcite fibres; each has a diameter of ~10 μm and the fibre length is parallel to the shell exterior. Detailed analyses of brachiopod shell calcite fibres, using electron back-scatter diffraction (EBSD) and atomic force microscopy (AFM), reveal the extent of the biological control.

Results and discussion

The calcite fibres of the secondary layer are parallel to the shell exterior. Electron backscatter diffraction (EBSD) reveals that the fibres are effectively single crystals with the calcite *c* axis perpendicular to the fibre axis (Fig. 2) (Schmahl *et al.*, 2004; Cusack *et al.*, 2007). Thus, as fibres grow, the crystallographic orientation of each fibre is maintained. The granular nature of the fibres is evident in the AFM images (Fig. 3) where the addition of bands of calcite granules to the growing fibre is clear. These bands of granules are thus added over the duration of fibre growth with uniform crystallographic orientation. The calcite fibres of Rhynchonelliform brachiopods

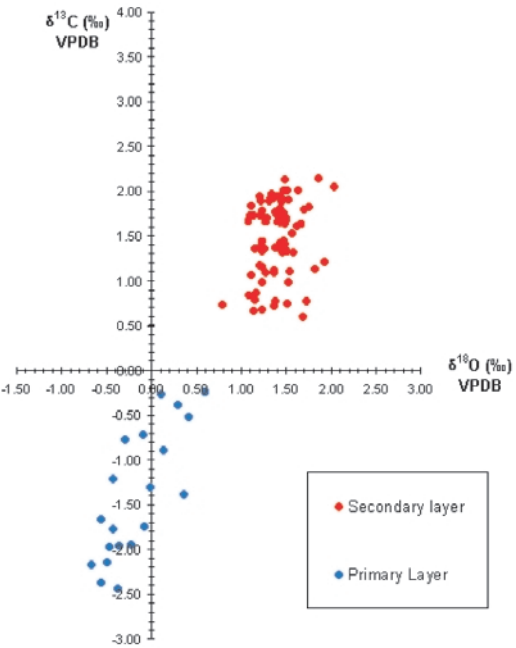

Fig. 1. $\delta^{18}O$–$\delta^{13}C$ crossplot of *Calloria inconspicua.*

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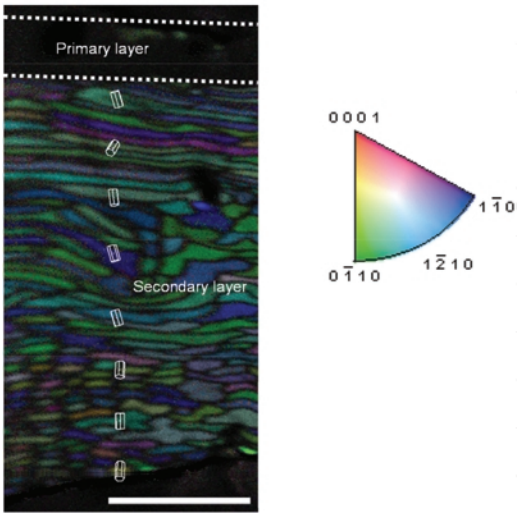

FIG. 2. Crystallographic orientation map of calcite fibres of *T. retusa* shell. Crystallographic orientation indicated by the colour key. This indicates that the calcite plane is normal to the field of view. White wire frames indicate the orientation of the unit cell. The outer (primary layer) and shell exterior are to the top of the image (not shown). Scale bar = 50 μm.

are not unique in terms of biomineral structures composed of nano-granules that collectively form what are essentially single crystals.

This phenomenon occurs in other biogenic carbonate structures such as tablets of aragonite nacre (Rousseau *et al.*, 2005; Addadi *et al.*, 2006; Nudelman *et al.*, 2007) and calcite prisms in molluscs (Nudelman *et al.*, 2007). Such granules occur in many phyla and, overall, the size range is constrained (Dauphin *et al.*, 2007). The aragonite granules of the cephalopod *Nautilus* are 40–50 nm in diameter (Dauphin *et al.*, 2007). Granules of similar dimensions to those of *Nautilus*, comprise the calcite prismatic layer of *Pinna* and *Pinctada* (Bivalvia) (Dauphin, 2003) and the aragonite crossed lamellar layers and calcite prisms of *Concholepas* and *Haliotis* (Dauphin, 2003). Such granules are also present in the aragonite skeletons of Scleractinia corals (Cuif and Dauphin, 2005: Dauphin, 2006) and in the calcite skeletons of *Octocorallia* (Dauphin, 2006).

These granules in *T. retusa* are 600 nm long and therefore larger than in other calcium carbonate biominerals. The factors that determine the dimension of the granules are unknown. The shape of the brachiopod granules are also different form those of mollusc shells or coral skeletons. Brachiopod granules are more triangular than those of molluscs or corals, and the sharp end of a granule is inserted in the hollow large part of the underlying granule (Fig. 4*b*). The large size and indeed shape of *T. retusa* calcite granules is intriguing and it remains to be determined whether or not this is a general feature of brachiopod calcite or unique to *T. retusa*. It raises the question of what factors determine the size of granules and why brachiopods, or *T. retusa* at least, should have larger granules than those in other calcite and aragonite biominerals.

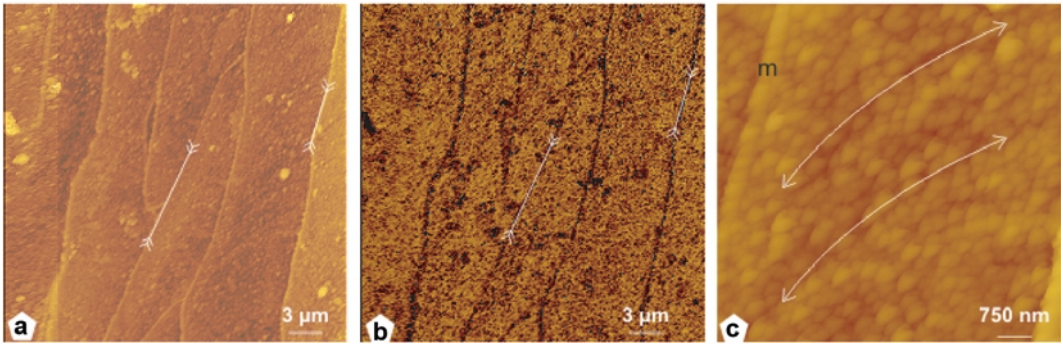

FIG. 3. Low magnification AFM images of a polished and etched section of *T. retusa* shell. (*a*) Low magnification height image showing the juxtaposition of several fibres separated by thin zones (arrows). (*b*) Phase image of the same zone, which shows the fibre margins (dark zone) have different physical and/or chemical properties relative to the inner part of the fibres. (*c*) Height image showing the detail of a fibre, with the granular structure and growth lines (arrows) clearly visible.

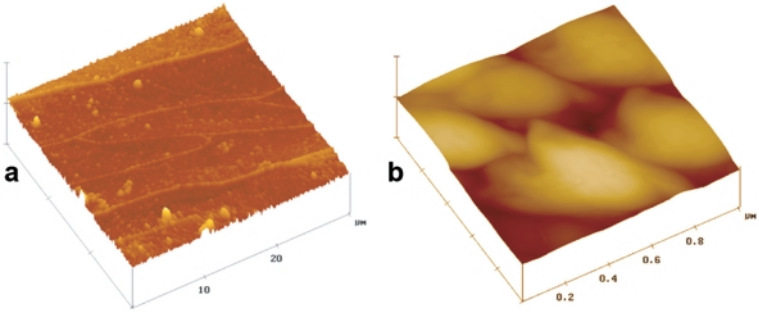

FIG. 4. (*a*) Three dimensional AFM images of *T. retusa* fibres; and (*b*) constituent granules.

Conclusions

The extent of the biological control exerted on the formation of the hierarchical structure of the calcite fibres is evident. The shape and dimensions of the granules are constrained as is their crystallographic alignment within the fibres. The dimensions and orientations of the fibres are also well constrained. Although there remains much to be understood about how this precise biological control is achieved, the attainment of isotope equilibrium under such strict biological influence is counter-intuitive.

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